OFFICE OF NAVAL RESEARCH
CONTRACT N00014-82-K-0322
Task No. NR P00 007

TECHNICAL REPORT NO. 27

STOICHIOMETRIC AND CATALYTIC RING OPENING OF HEXAALKYLCYCLODISILAZANES BY ORGANOALKALI REAGENTS

by

Dietmar Seyferth, Joanne M. Schwark and Regina M. Stewart

To be published in

"Organometallics"

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

May 13, 1989

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release. Distribution unlimited.
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 27	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Massachusetts Institute of Technology 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry 77 Massachusetts Avenue Cambridge, MA 02139	7b. ADDRESS (City, State, and ZIP Code) Department of Navy Arlington, VA 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) Department of Navy Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. N-00014-82 / PROJECT NO. K-0332 / TASK NO. P00007 / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
STOICHIOMETRIC AND CATALYTIC RING OPENING OF HEXAALKYLCYCLODISILAZANES BY ORGANOALKALI REAGENTS unclassified

12. PERSONAL AUTHOR(S)
Dietmar Seyferth, Joanne M. Schwark, and Regina M. Stewart

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Preprint	FROM ____ TO ____	1989-5-13	

16. SUPPLEMENTARY NOTATION
Manuscript "Organometallics"

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP
/		
/		

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
preceramic polymers, ceramic materials, polysilazanes, silanes, polysilanes, polymers

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The action of organoalkali reagents (RLi, RLi/Me_3CONa, RLi/Me_3COK) on cyclo-$(Me_2SiNMe)_2$ and cyclo-$(Me_2SiNPr^i)_2$ results in ring opening to give alkali metal amides of the type $RMe_2SiNMeSiMe_2NMeM$ (M= Li, Na, K) which react with chlorosilanes, $R'Me_2SiCl$, to give the expected linear trisilazanes. Relatively unhindered lithium amides also open the cyclo-$(Me_2SiNMe)_2$ ring. The use of a catalytic amount of RLi or RLi/Me_3CONa (but not of RLi/Me_3COK) results in ring opening polymerization of cyclo-$(Me_2SiNMe)_2$ but not of the more hindered cyclo-$(Me_2SiNPr^i)_2$.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. K.J. Wynne	22b. TELEPHONE (Include Area Code) 202/696-4410 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

STOICHIOMETRIC AND CATALYTIC RING OPENING OF HEXAALKYLCYCLODISILAZANES BY ORGANOALKALI REAGENTS.

Dietmar Seyferth*, Joanne M. Schwark and Regina M. Stewart

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ABSTRACT

The action of organoalkali reagents (RLi, RLi/Me_3CONa, RLi/Me_3COK) on cyclo-$(Me_2SiNMe)_2$ and cyclo-$(Me_2SiNPr^i)_2$ results in ring opening to give alkali metal amides of the type $RMe_2SiNMeSiMe_2NMeM$(M = Li, Na, K) which react with chlorosilanes, $R'Me_2SiCl$, to give the expected linear trisilazanes. Relatively unhindered lithium amides also open the cyclo-$(Me_2SiNMe)_2$ ring. The use of a catalytic amount of RLi or RLi/Me_3CONa (but not of RLi/Me_3COK) results in ring opening polymerization of cyclo-$(Me_2SiNMe)_2$ but not of the more hindered cyclo-$(Me_2SiNPr^i)_2$.

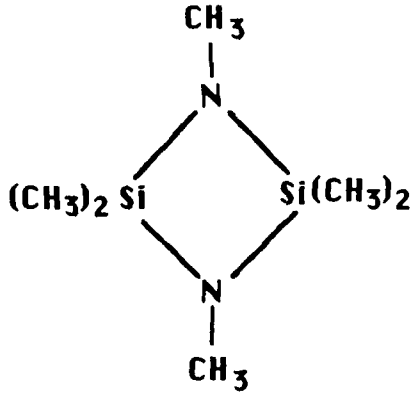
INTRODUCTION

Stoichiometric and catalytic ring opening of cyclotrisiloxanes by the action of strong nucleophilic reagents (OH^-, OR^-, $OSiMe_3^-$, RLi, etc.) is well known,[1] and the catalytic processes are useful in the preparation of linear polysiloxanes. Applied to cyclopolysilazanes, cyclo-$(R^1R^2SiNR^3)_n$, such processes might be expected to result in formation of linear polysilazanes. However, none have been reported thus far.[2] Our interest in polysilazanes as precursors for silicon nitride and silicon carbonitride[3] led us to investigate the possibility of organoalkali reagent-catalyzed ring opening polymerization of cyclic polysilazanes.

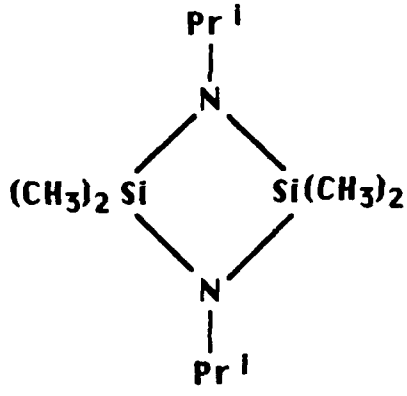
RESULTS AND DISCUSSION

In the cyclopolysiloxane series, cyclo-$(R_2SiO)_n$, the four-membered ring is known only when R is an extremely bulky organic group[4] and for the R = CH_3 series the cyclotrisiloxane is the smallest ring known. Hexamethylcyclotrisiloxane has enhanced reactivity, compared with the larger cyclics, and is readily cleaved by strong nucleophiles.[1] In the cyclopolysilazane series the four-membered-cyclodisilazane ring system is very stable, and many examples of Si_2N_2 rings have been reported.[5]

Before investigating the possibility of the catalytic ring opening polymerization of cyclodisilazanes we have studied the stoichiometric opening of the cyclodisilazane ring by organoalkali reagents. The cyclodisilazanes chosen for study were 1 and 2.



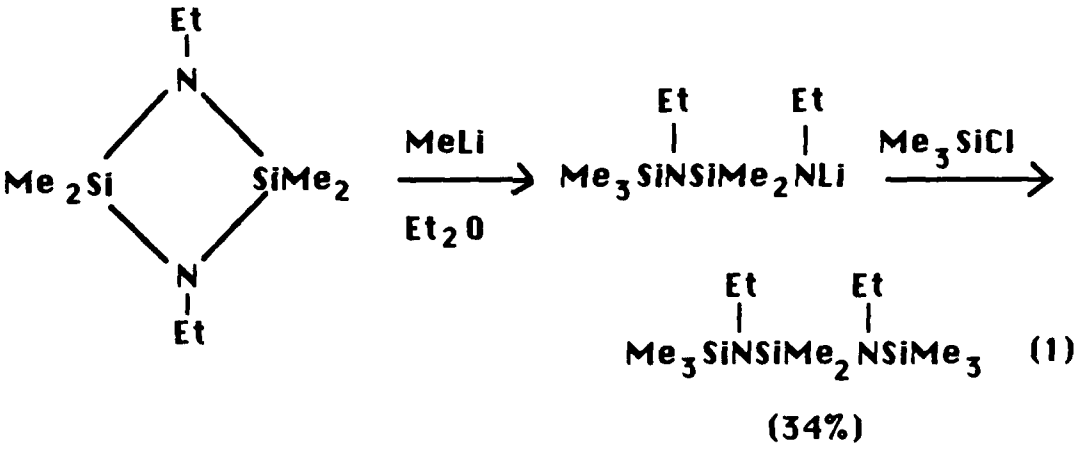
1



2

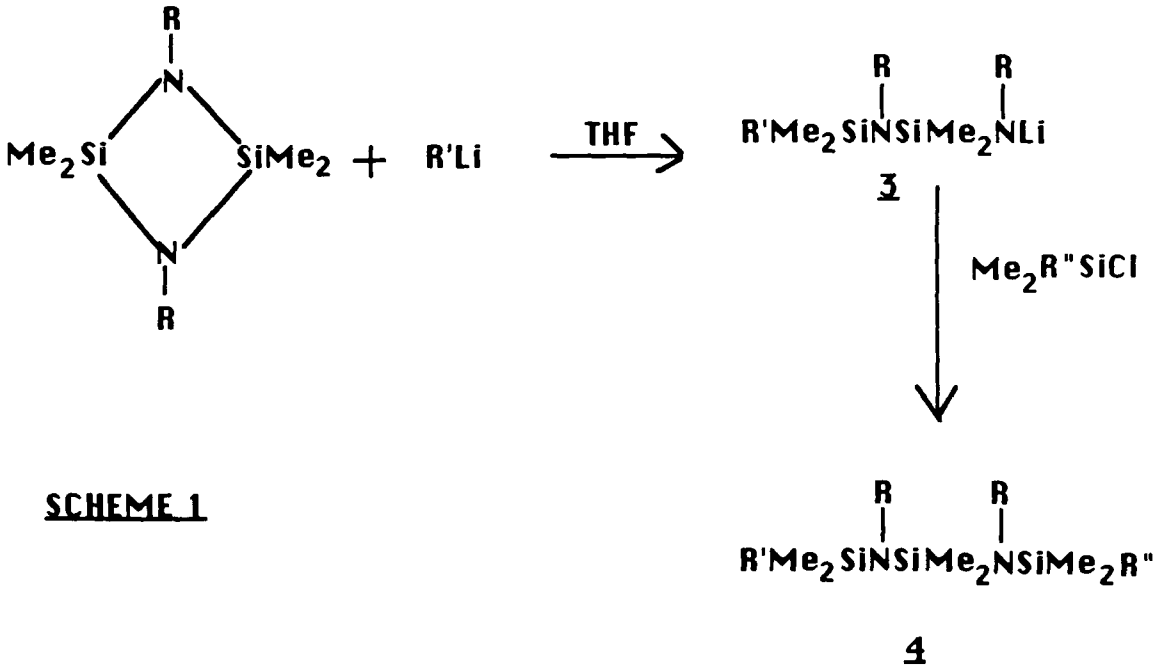
Both compounds are stable, distillable liquids. Hexamethylcyclodisilazane was found in a gas phase electron diffraction study to contain a planar Si_2N_2 ring, with an SiNSi angle of 98° and an Si-N bond distance of 1.74Å,[6] very similar to SiNSi bond angles and Si-N bond lengths of solid cyclodisilazanes as determined by X-ray diffraction.[7] It has been noted[5c] that the cyclodisilazane ring is quite strained compared with the six-membered cyclotrisilazane and the eight-membered cyclotetrasilazane rings. In view of this, one might expect that attack at a silicon atom of these cyclodisilazanes by a strongly nucleophilic organoalkali reagent will result in opening of the strained Si_2N_2 ring.

There has been one previous report of the cleavage of a cyclodisilazane by an organolithium reagent (eq. 1).[8] In our study of



such ring opening reactions we found such reactions of 1 and 2 to be fairly general in terms of the alkyllithium reagent that may be used (MeLi, n-BuLi, t-BuLi) and to proceed in high yield when carried out in THF solution (Table I and Scheme 1). In all reactions, the cyclodisilazane was added to a two- to fourfold excess of the respective organolithium reagent solution which had been cooled to a suitably low temperature (to minimize reaction of RLi with the solvent). The final reaction temperature depended on the lithium reagent used. Reactions with the reactive n- and t-butyllithium could be carried out at 0°C, but reactions with the less reactive methyllithium sometimes were carried out at room temperature or by heating briefly at reflux. The final quench with a chlorosilane was carried out at room

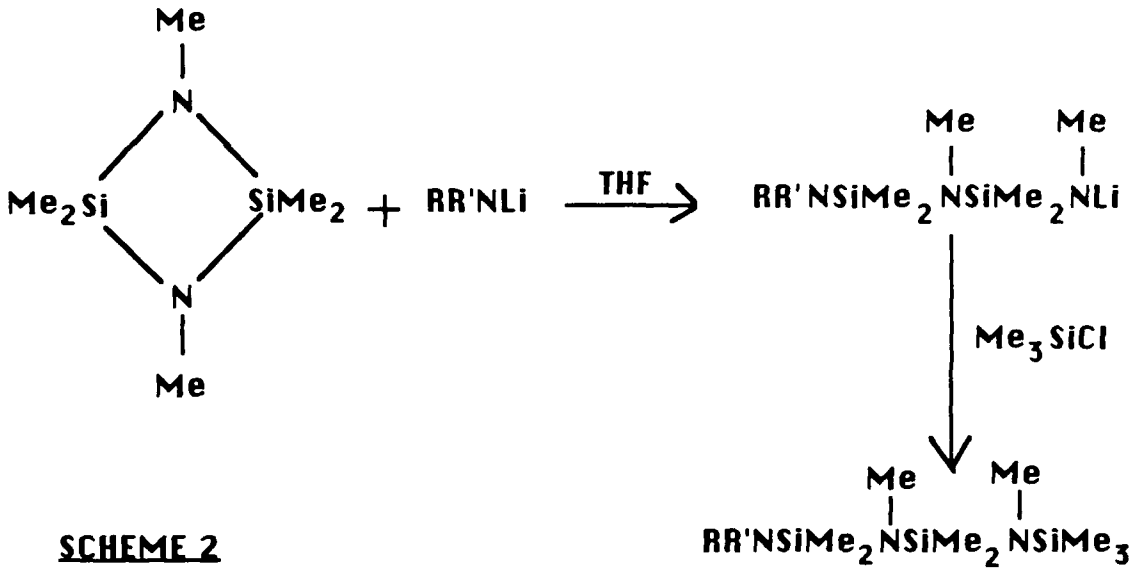
temperature or at reflux. In contrast to the facile ring opening of cyclo-$(Me_2SiO)_3$ by organolithium reagents and other strong nucleophiles,[1] cyclo-$(Me_2SiNMe)_3$ did not react with n-butyllithium in THF.



SCHEME 1

If cyclodisilazane ring opening is to be a useful oligomerization/polymerization procedure, the propagation steps involving further cyclodisilazane cleavage by lithium amide 3 and by higher oligomers and then polymers, i.e., by $R'[Me_2SiN(R)SiMe_2N(R)]_nLi$ in the case of cyclo-$(Me_2SiNMe)_2$, must occur at a reasonable rate. Such ring opening reactions were examined first in stoichiometric reactions (Scheme 2). They were found to proceed in good yield (R,R' = Me, 70%; R = Me; R' = Me_3Si, 83%) when the lithium amide was not too hindered and when the reaction mixture was heated at reflux. More hindered lithium amides such as iPr_2NLi and $(Me_3Si)_2NLi$ did not react with hexamethylcyclodisilazane. More to the point, a reaction of the initially formed methyllithium ring opening product, $Me_3SiNMeSiMe_2NMeLi$, with a second molar equivalent of hexamethylcyclodisilazane, i.e., the first propagation step, gave the expected $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeLi$ and addition of Me_3SiCl to the reaction mixture resulted in formation of $Me_3SiNMeSiMe_2NMeSiMe_3$

(4% yield) and $Me_3Si(NMeSiMe_2)_3NMeSiMe_3$ (25% yield), as well as higher, nonvolatile oligomers. Thus we could expect such polymerization to occur, at least with cyclo-$(Me_2SiNMe)_2$.



SCHEME 2

The initial ring-opening products, the lithium amides 3, appeared to be stable in solution, even in refluxing THF, at least for limited periods of time. A potential decomposition process of the type described by Fink[9] (eq. 2) was not observed. Apparently higher temperatures are required for such a cycloreversion process.

$$(Me_3Si)_2NSiMe_2N(SiMe_3)Li \xrightarrow[\text{reflux 8 h}]{\text{xylene}} LiN(SiMe_3)_2 + \text{cyclo-}(Me_2SiNSiMe_3)_2 \quad (2)$$

Lithium amide intermediates of type 3 could be observed by ^{29}Si NMR spectroscopy. A solution of $Me_3SiNMeSiMe_2NMeLi$ in which most of the THF had been removed by trap-to-trap distillation *in vacuo* and replaced by

C_6D_6 showed the ^{29}Si resonance (DEPT technique[10]) for the Me_3SiN silicon atom at δ_{Si} 2.53 and the $NSiMe_2NLi$ resonance at δ_{Si} -7.74. By comparison, the Me_3SiCl quench product of this lithium amide, $Me_3SiNMeSiMe_2NMeSiMe_3$ showed two ^{29}Si resonances at the δ_{Si} 5.35 (Me_3Si) and -0.26 ($SiMe_2$). (Hexamethylcyclodisilazane in C_6D_6 shows a single ^{29}Si resonance at 8.01 ppm). The ^{29}Si NMR spectra of this lithium amide and of n-$BuMe_2SiNMeSiMe_2NMeLi$ [δ_{Si} = 3.96 ($nBuMe_2SiN$) and -9.61 ($NSiMe_2N$)] were devoid of other resonances, an indication that a clean ring opening had taken place.

Organosodium and -potassium reagents in general are more reactive than organolithium reagents, so it was of interest to study the action of organosodium and -potassium nucleophiles on hexamethylcyclodisilazane. The sodium reagents chosen were of the Lochmann base type,[11] RLi/Me_3CONa. (R = n-Bu, Me). These react readily with hexamethylcyclodisilazane to give $RMe_2SiNMeSiMe_2NMeNa$ below room temperature. Subsequent reaction of these sodium amide intermediates with a chlorosilane gave good yields of linear trisilazanes.

Organopotassium reagents of the $MeLi/Me_3COK$ type[11] also reacted with hexamethylcyclodisilazane under mild conditions (-15°C). Addition of Me_3SiCl to such a reaction mixture gave $Me_3SiNMeSiMe_2NMeSiMe_3$ in 60% yield, in addition to some nonvolatile material.

Since stoichiometric ring opening of cyclo-$(Me_2SiNMe)_2$ by RLi, RNa and RK could be readily effected and since such cyclodisilazane ring opening also occurred with Me_2NLi and $Me_3Si(Me)NLi$, we undertook a study of organoalkali-catalyzed ring-opening polymerization of 1 and 2. The expected chemistry is shown in Scheme 3. If, as anticipated, the rate of initiation is much greater than the rates of the propagation steps, then the molecular weight of the product will be determined by the monomer/initiator molar ratio (in the absence of side reactions).

Catalytic ring opening polymerization of hexamethylcyclodisilazane by n-butyl- and methyllithium and -sodium did indeed occur. The required reaction temperatures reflected the reactivity of these organoalkali reagents in

the stoichiometric reactions. Thus, the RLi-initiated reactions were started at 0°C and then the reaction mixtures were heated at reflux (in THF) until no more cyclo-$(Me_2SiNMe)_2$ could be detected by GLC.. In the case of the RNa-initiated polymerizations, the cyclodisilazane was added to the RLi/Me_3CONa reagent at -78°C and subsequently the reaction mixture was warmed to -15°C and finally to room temperature. The products in general were white waxy solids. Their molecular weights, determined by cryoscopy in benzene, were in the 1000 - 3000 range and in most cases were not too far off from the theoretical molecular weight calculated from the monomer/catalyst molar ratio. However, cryoscopic molecular weights in that range are only approximate and no useful quantitative data are in hand. However, it is clear that ring-opening polymerization of hexamethylcyclodisilazane has been effected. Polymers of type $RMe_2SiNMe(SiMe_2NMe)_nSiMe_2R'$ with n = about 11 to 35 have been prepared.

The oligomeric/polymeric products obtained must be linear species of the type shown in Scheme 3. For instance, the ^1H NMR spectrum (in $CDCl_3$) of the wax obtained by the action of 5 mole % n-BuLi/Me_3CONa on cyclo-$(Me_2SiNMe)_2$ (Me_3SiCl quench) showed only two resonances at d 0.12 ($SiCH_3$) and 2.40 (NCH_3). The $\underline{n}$-C_4H_9 resonances were observed only when the spectrum intensity was increased by several orders of magnitude. The ^{29}Si NMR spectrum in $CDCl_3$ of the wax showed a single resonance at δ_{Si} -2.27. In contrast, the ^{29}Si NMR spectrum (in $CDCl_3$) of the product obtained by the action of 10 mole % MeLi/Me_3CONa on cyclo-$(Me_2SiNMe)_2$ (Me_3SiCl quench), which was of lower molecular weight (1425-1500), showed the resonances due to the terminal Me_3Si groups (5.17 ppm), the Me_2Si next to the Me_3Si groups (-1.53 ppm) and the Me_2Si groups further inward (-2.25 ppm). These values should be compared with the ^{29}Si NMR spectrum of $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeSiMe_3$ which was isolated as a pure compound and, in $CDCl_3$ solution, showed ^{29}Si resonances at δ_{Si} 4.97, -1.46 and -2.63).

It would appear that in the case of RK initiation of the ring-opening polymerization of hexamethylcyclodisilazane the propagation process (Scheme 3) is complicated by "back-biting" of the reactive potassium amide chain terminus, a process which results in extrusion of cyclo-$(Me_2SiNMe)_3$ as shown in Scheme 4 in its simplest form. Presumably, only the potassium

SCHEME 3

Initiation

$$RLi + \text{cyclo-}(Me_2SiNMe)_2 \longrightarrow RMe_2SiNMeSiMe_2NMeLi$$

Propagation

$$RMe_2SiNMeSiMe_2NMeLi + \text{cyclo-}(Me_2SiNMe)_2 \longrightarrow RMe_2SiNMe(SiMe_2NMe)_3Li$$

$$\downarrow \text{cyclo-}(Me_2SiNMe)_2$$

$$RMe_2SiNMe(SiMe_2NMe)_5Li$$

$$\downarrow \text{etc.}$$

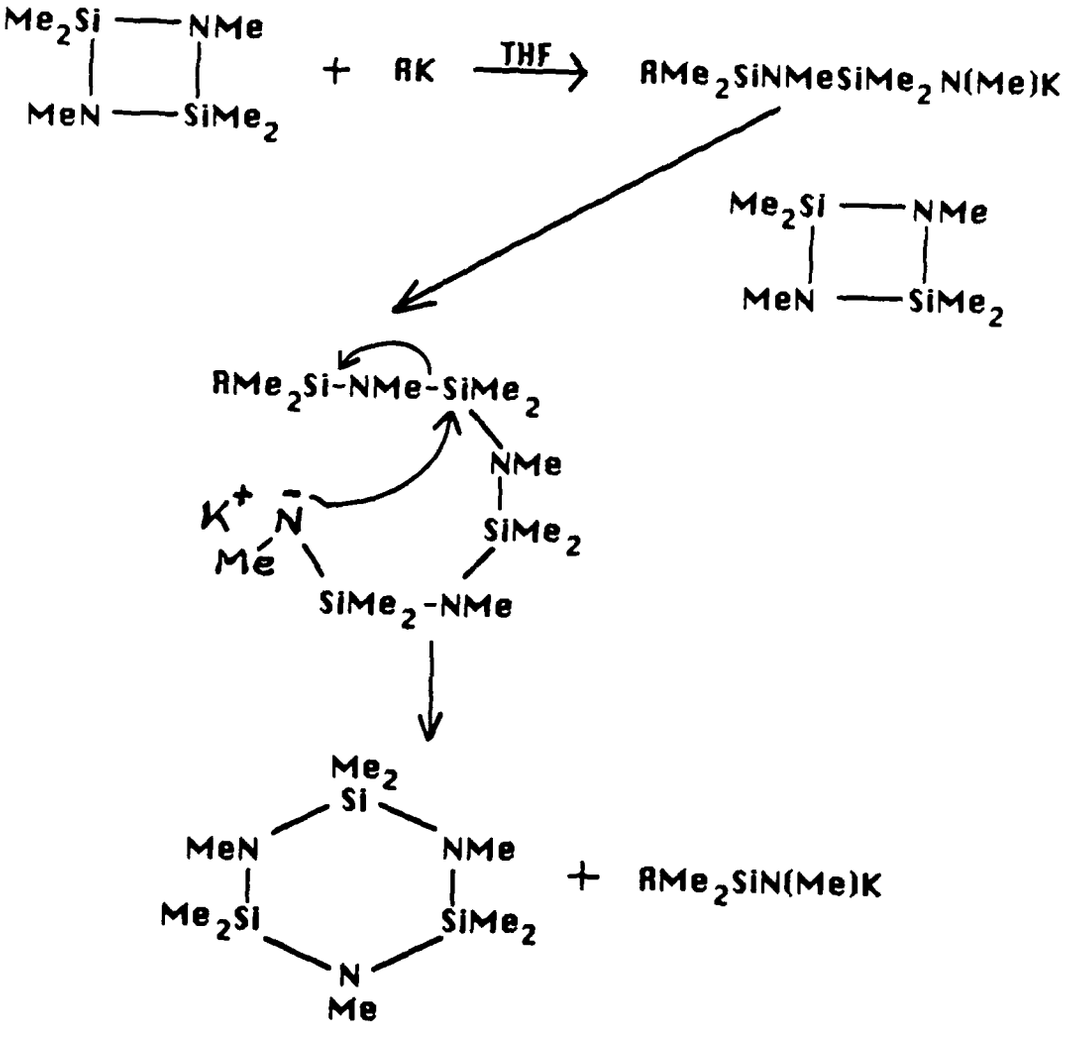
$$RMe_2SiNMe(SiMe_2NMe)_nLi$$

("living polymer")

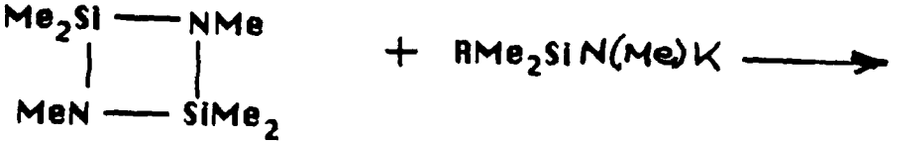
Termination

$$RMe_2SiNMe(SiMe_2NMe)_nLi + Me_2R'SiCl \longrightarrow RMe_2SiNMe(SiMe_2NMe)_nSiMe_2R'$$

SCHEME 4



then:



$RMe_2SiNMeSiMe_2NMeSiMe_2N(Me)K$

etc.

amide chain end (*vs.* lithium or sodium amide) is reactive enough to effect such nucleophilic chain scission.

The chemistry of the organoalkali-initiated ring opening polymerization of hexamethylcyclodisilazane does not appear to be a general process. The R_2NLi stoichiometric ring opening of cyclo-$(MeSiNMe)_2$ is, as mentioned above, subject to steric hindrance. Thus, it was not surprising that attempted ring opening polymerization of cyclo-$(Me_2SiNPr^i)_2$ by 5 mole % n-BuLi in THF at room temperature, then at reflux, was unsuccessful. Obviously, the initially formed $R'SiMe_2NPr^iSiMe_2N(Pr^i)Li$ intermediate is too hindered, so initiation is not followed by the propagation steps. Although this was not investigated, one would expect that bulky substituents on silicon also would prevent ring opening polymerization of cyclodisilazanes by RLi.

Linear organosilicon polymers do not give ceramic residues in high yield when they are pyrolyzed if they do not contain functional substituents whose thermally induced reactions lead to extensive cross-linking during the initial stages of pyrolysis. Linear polysilazanes of the type prepared in this study do not contain such substituents and thus it was not surprising that, as the TGA trace in Figure 1 shows, there is no ceramic residue when they are pyrolyzed. Thus, as expected, linear polysilazanes with an R_2SiNR' repeat unit are not useful preceramic polymers. Trapping of the volatile pyrolysis products of a $Me_3Si[NMeSiMe_2]_xNMeSiMe_3$ polymer showed them to consist of cyclo-$(Me_2SiNMe)_2$ and cyclo-$(Me_2SiNMe)_3$, with the former predominating. The formation of these small cyclics can be rationalized either in terms of (a) a radical chain scission/back-biting process or (b) of a decomposition to give an unsaturated $Me_2Si{=}NMe$ intermediate which then undergoes cycloaddition. It may be that the cyclic trimer is formed by process (a) and the cyclic dimer by process (b).

EXPERIMENTAL

General Comments.

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques or a nitrogen-filled Vacuum Atmospheres dry box. All solvents were distilled under nitrogen from the appropriate drying agents. Chlorosilanes were purchased from Petrarch Systems, Inc. or Silar, and distilled from magnesium chips before use. Methyl- and t-butyllithium were purchased from Aldrich. Organolithium reagents were titrated for RLi content by the Gilman double titration method· Unsolvated potassium tert-butoxide (Aldrich) and sodium tert-butoxide (Alfa) were used as received.

Gas chromatographic (GLC) analyses were performed on a Hewlett-Packard 5890A gas chromatograph equipped with a 6 ft, 0.25 in column packed with 10% SE-30 silicone rubber gum on Chromosorb P. The internal standard method was used in yield determinations with a temperature program of 6°C/min from 100-275°C. Internal standards used were octane (C_8), nonane (C_9), decane (C_{10}). Preparative GLC (Gow Mac 550 Thermal Conductivity Detector Gas Chromatograph, 6 ft, 0.25 in 10% SE-30 on Chromosorb P column) was used to collect samples for analysis and spectroscopy.

Proton NMR spectra were obtained either with a Jeol FX-90Q, a Bruker WM-250 or Varian XL-300 NMR spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from tetramethylsilane. ^{29}Si NMR spectra (fully proton decoupled) were obtained using a Varian XL-300 operating at 59.59 MHz in $CDCl_3$ or C_6D_6 with 0.05 M $Cr(acac)_3$ as a relaxation reagent. Tetramethylsilane (at 0.00 ppm) was used as an external standard. As indicated in the experiments below, some ^{29}Si NMR spectra were obtained using a DEPT pulse sequence.[10]

Molecular weights were determined by cryoscopy in benzene at M.I.T. or by vapor pressure osmometry by Galbraith Laboratories, Knoxville, TN. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

For the polymers, the "theoretical" analytical values are those calculated on the basis of the experimental molecular weights. Since the latter were only approximate, the agreement between calculated and found analytical values was not always good.

Preparation of Starting Materials.

(a) Dimethylbis(methylamino)silane. A 1 l, three-necked flask equipped with a septum, an overhead mechanical stirrer and a cold condenser (Dry Ice/acetone) was flame-dried under nitrogen and charged with 85.1 g (0.66 mol) of Me_2SiCl_2 and 400 ml of diethyl ether and cooled to 0°C. Gaseous methylamine (Matheson) was bubbled into the solution through a 6 in. stainless steel needle during the course of 3 h. The reaction mixture was allowed to warm to room temperature overnight. The precipitated $[MeNH_3]Cl$ was filtered under nitrogen and washed with two 50 ml portions of ether. The combined organic phase was distilled to remove the Et_2O. The residue was distilled (1 ft. Vigreux column) to give 48.8 g (63%) of $Me_2Si(NHMe)_2$, bp 109°C (lit[12] bp 57-58°C at 132 mm Hg).
^1H NMR (90 MHz, $CDCl_3$): δ -0.07 (s, 6H, Me_2Si), 0.44 (broad s, 2H, NH), 2.41 (s, 6H, NMe).

(b) Dimethylbis(isopropylamino)silane.

A similar reaction in which 26.2 g (0.2 mol) of Me_2SiCl_2 was added to 52.7g (0.89 mol) of isopropylamine (Aldrich, distilled from CaO) in 400 ml of Et_2O gave 28.9 g (82%) of $Me_2Si(NHPr^i)_2$ bp 44°C/10 mm Hg). (lit.[13] bp 47-48°C/11 mm Hg).
^1H NMR (90 MHz, $CDCl_3$): δ -0.02 (s, 6H, Me_2Si), 1.02 (d, J = 6.7 Hz, 12H, Me_2C), 3.20 (broad m, 2H, NC<u>H</u>).

(c) Hexamethylcyclodisilazane.

A 1 l three-necked flask equipped with a mechanical stirrer, a condenser topped with a gas inlet tube (connecting to an oil bubbler in a Schlenk line), and a septum was flame dried and charged with 24.73 g (0.21

mol) of $Me_2Si(NHMe)_2$ and 62 ml of hexane. By means of a 250 ml addition funnel 277 ml of 1.51 M "halide-free" methyllithium (0.42 mol) was added at 0°C, dropwise over 2 h. After the mixture had been stirred at 0°C for 2h, 26.9 g (0.21 mol) of Me_2SiCl_2 was added dropwise at 0°C. The reaction mixture was stirred and heated at reflux for 24 h. Filtration (or centrifugation) removed the LiCl. Removal of the solvent by trap-to-trap distillation (room temperature, 70 mm Hg) was followed by distillation of the product, 23.8 (65%) of cyclo-$(Me_2SiNMe)_2$, bp 50°C/50mm Hg or 60-62°C at 70 mm Hg (lit.[12] bp 52-52.5°C at 51 mm Hg).

^1H NMR (90 MHz, $CDCl_3$): δ 0.12 (s, 12H, $SiMe_2$), 2.42 (s, 6H, MeN). ^{13}C NMR (67.9 MHz, C_6D_6): δ_c 0.44 (q, J=117.0 Hz, Me_2Si), 26.87 (q, J=134.9 Hz, MeN). ^{29}Si NMR (59.59 MHz, C_6D_6, DEPT): δ_{Si} 8.06 IR (thin film): 2955(m), 2900(s), 2810(s), 1435(vw), 1250(vs), 1190(vs), 860(vs), 840(sh), 785(vs), 675(vw), cm^{-1}.

(d) N,N'-Diisopropyltetramethylcyclodisilazane.

The reaction flask was charged with 15.06 g (0.086 mol) of $Me_2Si(NHPr^i)_2$ and 250 ml of Et_2O. n-Butyllithium (65 ml of 2.68M in hexane, 0.173 mol) was added. After the resulting solution had been heated at reflux for 30 min, 11.2 g (0.087 mol) of Me_2SiCl_2 was added. The reaction mixture was stirred and heated at reflux for 3 h, then was centrifuged to separate the LiCl. The organic layer, after removal of the Et_2O, was distilled (1 ft Vigreux column) to give 16.3 g (82%) of cyclo-$(Me_2SiNPr^i)_2$, bp 48.5/2.5 mm Hg.

^1H NMR (90 MHz, $CDCl_3$): δ 0.19 (s, 12H, Me_2Si), 1.01 (d, J=6.3Hz, 12H, Me_2C), 3.19 (sept, J=6.3 Hz, 2H, NCH), which agrees with the literature.[15]

Reaction of cyclo-$(Me_2SiNMe)_2$ with Methyllithium.

(a) Trimethylchlorosilane Quench

A 50 ml three-necked, round-bottomed flask equipped with a condenser topped with a gas inlet/outlet tube connected to an oil bubbler in a Schlenk line, a stir-bar, a glass stopper, and a septum (henceforth, the "standard reaction apparatus") was flame-dried and charged with 30 ml of THF and 13.0 ml of 1.51 M methyllithium (LiBr complex) (19.6 mmol) in diethyl ether. This solution was heated to reflux and 0.873 g (5.0 mmol) of cyclo-$(Me_2SiNMe)_2$ was added dropwise by syringe during the course of 20 min. The resulting solution was heated at reflux for 25 min. and then 5.36 g (49.3 mmol) of Me_3SiCl was added. The reaction mixture was stirred and heated at reflux for 30 min. At this point, a GLC yield determination was carried out. The solvent then was removed by trap-to-trap distillation (room temperature in vacuum). The residue was extracted with 20 ml of hexane and the extracts were filtered to remove LiCl. Distillation of the hexane left an oily residue from which the product was isolated by GLC (this is the "standard workup"). The GLC analysis (C_8 internal standard) showed the presence of one major product, identified as $Me_3SiNMeSiMe_2NMeSiMe_3$, in 70% yield.

Anal. Calcd. for $C_{10}H_{30}N_2Si_3$: C, 45.74; H, 11.51; N, 10.69. Found: C, 45.50; H, 11.33; N, 10.87.

^1H NMR (90 MHz, $CDCl_3$): δ 0.05 (s, 18H, Me_3Si), 0.07 (s, 6H, Me_2Si), 2.40 (s, 6H, MeN).

(b) Dimethylchlorosilane Quench

The same procedure, with the exception that Me_2SiHCl was the chlorosilane used, gave $Me_3SiNMeSiMe_2NMeSiMe_2H$ in 83% yield.

Anal. Calcd. for $C_9H_{28}N_2Si_3$: C, 43.48; H, 11.35; N, 11.27. Found: C, 43.57; H, 11.39; N, 11.30.

^1H NMR (90 MHz, $CDCl_3$): δ 0.06 (s, 9H, Me_3Si), 0.07 (s, 6H, NMe_2SiN), 0.09 (d, J=3.4 Hz, 6H, Me_2SiH), 2.39, 2.41 (both s, 6H, MeN), 4.42 (sept, J=3.4 Hz, Me_2SiH).

(c) Dimethyldichlorosilane Quench

The same procedure was used except that Me_2SiCl_2 (an excess) was the chlorosilane added at the end. The product, $Me_3SiNMeSiMe_2NMeSiMe_2Cl$, was obtained in 57% yield.

Anal.. Calcd for $C_9H_{27}N_2Cl\ Si_3$: C, 38.19; H, 9.62; N, 9.90. Found: C, 38.54; H, 9.63; N, 9.92.

^1H NMR (250 MHz, $CDCl_3$): δ 0.069 (s, 9H, $SiMe_3$), 0.15 (s, 6H, $SiMe_2$), 0.46 (s, 6H, $SiMe_2Cl$), 2.42 (s, 3H, NMe), 2.49(s, 3H, NMe).

Reaction of this compound with an excess of CH_3NH_2 in hexane at -78°C gave $Me_3SiNMeSiMe_2NMeSiMe_2NHMe$ in 79% yield.

Anal. Calcd. for $C_{10}H_{31}N_3Si_3$: C, 43.26; H, 11.26; N, 15.13. Found: C, 43.43; H, 11.17; N, 15.11.

^1H NMR (250 MHz, $CDCl_3$): δ 0.052 (s, 6H, $SiMe_2$), 0.056 (s, 9H, $SiMe_3$), 0.100 (s, 6H, $SiMe_2$), 2.41 (s, 9H, NCH_3).

Reaction of cyclo-$(Me_2SiNMe)_2$ with n-Butyllithium.

(a) Trimethylchlorosilane Quench

The standard reaction apparatus was charged with 30 ml of THF, cooled to 0°C and then 9.0 ml of 2.58M n-butyllithium (23.2 mmol) in hexane was added. Subsequently, 1.28 g (7.33 mmol) of cyclo-$(Me_2SiNMe)_2$ was added. The reaction mixture was stirred at 0°C for 30 min and then 4.29 g (39.5 mmol) of Me_3SiCl was added by syringe. The resulting reaction mixture, from which LiCl had precipitated, was warmed to room temperature. The standard workup followed. The product, n-$BuMe_2SiNMeSiMe_2NMeSiMe_3$, was obtained in 81% yield.

Anal. Calcd. for $C_{13}H_{36}N_2Si_3$: C, 51.24; H, 11.91; N, 9.19. Found: C, 51.30; H, 11. 90; N, 9.38.

^1H NMR (90MHz, $CDCl_3$): δ 0.04 (s, 6H, n-BuMe_2Si, 0.06 (s, 9H, Me_3SiN), 0.08 (s, 6H, $NSiMe_2N$), 0.68 - 1.42 (complex m, 9H, n-Bu), 2.40 (s, 6H, MeN),

(b) Dimethylchlorosilane Quench

The same procedure was used, but Me_2SiHCl was added to the end rather than Me_3SiCl. The product, n-$BuMe_2SiNMeSiMe_2$-$NMeSiMe_2H$, was obtained in 86% yield.

Anal. Calcd. for $C_{12}H_{34}N_2Si_3$: C, 49.76; H, 11.48; N, 9.67. Found: C, 49.73, H, 11.84; N, 9.44..

^1H NMR (90 MHz, $CDCl_3$): δ 0.04(s, 6H, n-Bu$\underline{Me_2}$Si), 0.07 (s, 6H, $NSiMe_2N$), 0.10 (d, J = 2.9 Hz, 6H, Si$\underline{Me_2}$H), 0.68-1.42 (complex m, 9H, n-Bu), 2.39, 2.40 (both s, 6H, MeN), 4.43 (complex m, 1H, $Me_2Si\underline{H}$)

Reaction of cyclo-$(Me_2SiNMe)_2$ with with t-Butyllithium.

(a) Trimethylchlorosilane Quench

The standard reaction apparatus was charged with 30 ml of THF, and cooled to -78°C (Dry Ice/Me_2CO). and 10.0 ml of a 2.10$\underline{M}$ solution of t-butyllithium (21.0 mmol) in pentane was added. By syringe, 1.32 g (7.56 mmol) of cyclo-$(Me_2SiNMe)_2$ was added The mixture was stirred at -78°C for 30 min and then the -78°C bath was replaced with an ice bath. After the mixture had been stirred at 0°C for 30 min., 4.29 g (39.5 mmol) of Me_3SiCl was added. The reaction mixture was warmed to room temperature. The standard workup showed that the expected product, t-$BuMe_2SiNMeSiMe_2NMeSiMe_3$, had been formed in 87% yield.

Anal. Calcd. for $C_{13}H_{36}N_2Si_3$: C, 51.24; H, 11.91; N, 9.19. Found: C, 51.31; H, 11.91; N, 9.09.

^1H NMR (90 MHz, $CDCl_3$): δ 0.05(s, 15H, t-Bu$\underline{Me_2}$Si and Me_3Si), 0.10 (s, 6H, $NSiMe_2N$), 0.86 (s, 9H, t-Bu), 2.41, 2.44 (both s, 6H, MeN).

(b) Dimethylchlorosilane Quench

The same procedure, except that Me_2SiHCl was used instead of Me_3SiCl, gave t-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ in 80% yield.
Anal. Calcd. for $C_{12}H_{34}N_2Si_3$: C, 49.76; H, 11.48; N, 9.67. Found: C, 49.60; H, 11.83; N, 9.41.
^1H NMR (90 MHz, $CDCl_3$): δ 0.10 (d, J=3.2 Hz, 6H, Me_2SiH), 0.10 (s, 6H, t-$BuMe_2Si$), 0.19 (s, 6H, $NSiMe_2N$), 0.91 (s, 9H, t-Bu), 2.32, 2.41 (both s, 6H, MeN), 4.67 (sept, J = 3.2Hz, 1H, Me_2SiH).

Reaction of cyclo-$(Me_2SiNMe)_2$ with Lithium Dimethylamide.

The standard reaction apparatus was charged with 20 ml of THF and cooled to -78°C (Dry Ice/Me_2CO). Dimethylamine (3ml liquid, 2.04 g, 0.045 mol) at -78°C was cannulated into the reaction flask. By syringe, 3.70 ml of a 2.32M solution of n-BuLi (8.60 mmol) in hexane was added to this solution. The resulting Me_2NLi solution was warmed to room temperature, then was heated to reflux and 0.923 g (5.29 mmol) of cyclo-$(Me_2SiNMe)_2$ was added by syringe, dropwise during the course of 20 min. The reaction mixture was cooled to room temperature and 1.03 g (9.47 mmol) of Me_3SiCl was added. The standard workup followed. The product, $Me_2NSiMe_2NMeSiMe_2NMeSiMe_3$, was obtained in 70% yield.
Anal. Calcd. for $C_{11}H_{33}N_3Si_3$: C, 45.30; H, 11.40; N, 14.41. Found: C, 45.02; H, 11.60; N, 14.36.
^1H NMR (250 MHz, $CDCl_3$): δ 0.17 (s, 12H, $NSiMe_2N$), 0.20 (s, 9H, Me_3Si), 2.40, 2.42 (both s, 6H, SiNMeSi), 2.44 (s, 6H, Me_2N).

Reaction of cyclo-$(Me_2SiNMe)_2$ with Lithium N-Methyltrimethylsilylamide.

The standard reaction apparatus was charged with 20 ml of THF and 0.786 g (7.61 mmol) of $Me_3SiNHMe$ and cooled to -78°C. By syringe, 3.28 ml of a 2.32M solution of n-BuLi in hexane (5.15 mmol) was added . After the mixture had been stirred for 10 min at -78°C it was warmed to room temperature and then heated to reflux. Hexamethylcyclodisilazane (0.9 g, 5.15 mmol) was added dropwise by syringe. After the mixture had been stirred for

30 min at reflux, 1.03 g (9.47 mmol) of Me_3SiCl was added. The standard workup followed. The product, $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_3$, was obtained in 83% yield.

Anal. Calcd. for $C_{13}H_{39}N_3Si_4$: C, 44.63; H, 11.24; N, 12.01. Found: C, 44.84; H, 11.18; N, 12.13.

^1H NMR (90 MHz, C_6D_6): δ 0.19 (s, 18H, Me_3Si), 0.25 (s, 12H, $NSiMe_2N$), 2.44 (s, 9H, MeN).

Reaction of cyclo-$(Me_2SiNMe)_2$ with $Me_3SiNMeSiMe_2NMeLi$.

The standard reaction apparatus was charged with 25 ml of THF and cooled to 0°C. By syringe, 3.0 ml of a 1.35M solution of methyllithium (4.05 mmol) in Et_2O was added. Subsequently, 0.711 g (4.08 mmol) of cyclo-$(Me_2SiNMe)_2$ was added to the MeLi solution, dropwise over 10 min. The resulting solution was stirred for 20 min at 0°C and then for 30 min. at reflux. Another portion (0.60 g, 3.44 mmol) of cyclo-$(Me_2SiNMe)_2$ then was added. After this solution had been heated for 30 min. at reflux, it was cooled to room termperature and 3.0 ml (23.7 mmol) of Me_3SiCl was added. After 30 min. at room temperature the standard workup was done. GLC analysis (C_9 internal standard) showed the presence of two volatile products: $Me_3SiNMeSiMe_2NMeSiMe_3$ (14%), identified by its ^1H NMR spectrum (see above), and the pentasilazane, $Me_3SiNMeSiMe_2NMeSiMe_2NMeSiMe_2NMeSiMe_3$ (25%). The latter was isolated by GLC and characterized.

Anal. Calcd. for $C_{16}H_{48}N_4Si_5$: C, 43.98; H, 11.07; N, 12.82. Found: C, 43.84; H, 11.00; N, 13.08.

^1H NMR (250 MHz, $CDCl_3$): δ 0.05 (s, 18H, Me_3Si), 0.07 (s, 18H, Me_2Si), 2.4 (s, 12H, MeN).

^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} -2.63 (s, 1 Si, $SiMe_2$ central), -1.46 (s, 2 Si, $SiMe_2$ first from end), 4.97 (s, 2 Si, Me_3Si).

Reaction of cyclo-$(Me_2SiNPr^i)_2$ with Methyllithium.

The standard reaction apparatus was charged with 25 ml of THF and 2.50 ml. of a 1.66M solution of MeLi in Et_2O (4.15 mmol). This solution was heated to reflux and 0.430 g (1.87 mmol) of cyclo-$(Me_2SiNPr^i)_2$ was added. After the mixture had been stirred and heated at reflux for 30 min , 0.85 g (9.0 mmol) of Me_2SiHCl was added. The standard workup followed. The product, $Me_3SiNPr^iSiMe_2NPr^iSiMe_2H$, was obtained in 64% yield.

Anal. Calcd. for $C_{13}H_{36}N_2Si_3$: C, 51.26; H, 11.91; N, 9.20. Found: C, 51.37; H, 11.90; N, 9.32.

^1H NMR (250 MHz, $CDCl_3$): δ 0.14 (s, 9H, Me_3Si), 0.17 (d, J=3.6Hz, 6H, Me_2SiH), 0.19 (s, 6H, $NSiMe_2N$), 1.15 (d, J=6.7Hz, 6H, Me_2CH), 1.17 (d, J=6.7Hz, 6H, Me_2CH, 3.46 (sept, J=6.7Hz, 2H, Me_2CH), 4.53 (sept, J = 3.7 Hz, Me_2SiH).

Reaction of cyclo-$(Me_2SiNPr^i)_2$ with n-Butyllithium.

Using the same procedure, the reaction of 0.865 g (3.76 mmol) of cyclo-$(Me_2SiNPr^i)_2$ in 25 ml of THF with 4.20 mmol of n-BuLi in hexane was carried out at room temperature. Addition of 0.87 g (9.20 mmol) of Me_2SiHCl and the standard workup followed. The product, n-$BuMe_2SiNPr^iSiMe_2NPr^iSiMe_2H$, was obtained in 67% yield.

Anal. Calcd. for $C_{16}H_{42}N_2Si_3$: C, 55.42; H, 12.21; N, 8.08. Found: C, 55.34; H, 12.14; N, 8.20.

^1H NMR (250 MHz, $CDCl_3$): δ 0.13 (s, 6H, n-BuMe_2Si), 0.17 (d, J = 3.6 Hz, 6H, Me_2SiH), 0.20 (s, 6H, $NSiMe_2N$), 0.60 - 1.42 (complex m, 9H, n-Bu), 1.15 , 1.17 (both d, J=6.7Hz, 12H, Me_2CH), 3.47 (sept, J=6.7Hz, 12H, Me_2CH), 4.53 (sept, J=3.6 Hz, 1H, Me_2SiH).

A trimethylchlorosilane quench of such a cyclo-$(Me_2SiNPr^i)_2$/n-BuLi reaction mixture gave n-$BuMe_2SiNPr^iSiMe_2NPr^iSiMe_3$ in 60% yield.

Anal. Calcd. for $C_{17}H_{44}N_2Si_3$: C, 56.59; H, 12.29; N, 7.76. Found: C, 56.50; H, 12.28; N, 7.84.

^1H NMR (250 MHz, $CDCl_3$): δ 0.14 (s, 6H, n-BuMe_2Si), 0.15 (s, 9H, Me_3Si), 0.21 (s, 6H, $NSiMe_2N$), 0.60 - 1.42 (complex m, 9H, n-Bu) 1.17 (d, J=6.0Hz, 12H, Me_2CH), 3.52, 3.57 (both sept, J=6.0 Hz, 2H, Me_2CH).

Attempted Reaction of cyclo-$(Me_2SiNMe)_2$ with Lithium Bis(trimethylsilyl)amide.

The standard reaction apparatus was charged with 20 ml of THF, and 2.50 ml. of $(Me_3Si)_2NH$ (1.93 g, 0.012 mol) and cooled to -78°C in a dry ice/acetone bath. By syringe, 4.50 ml of a 2.66M solution of n-butyllithium (12.0 mmol) in hexane was added over 5 min. The dry ice/acetone bath was removed after 15 min and the reaction mixture was warmed to room temperature, then heated to reflux. By syringe, cyclo-$(Me_2SiNMe)_2$ (0.961 g, 5.51 mmol) was added dropwise over 30 min. After an additional 16h at reflux, the reaction mixture was cooled to room temperature and trimethylchlorosilane (1.58 ml, 1.36 g, 12.50 mmol) was added. A white precipitate formed. The GLC analysis (internal standard C_9) of the reaction mixture showed the presence of unreacted $(Me_2SiNMe)_2$ in 100% yield, which was identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

Reaction of cyclo-$(Me_2SiNMe)_2$ with n-Butyllithium/Sodium t-Butoxide.

(a) Trimethylchlorosilane Quench

The standard apparatus, equipped also with a low temperature themometer, was charged with 0.905 (9.42 mmol) of t-BuONa and 40 ml of THF, and, after cooling to -78°C, 3.66 ml of a 2.57M solution of n-BuLi in hexane (9.42 mmol). After 5 minutes, 0.816 g (4.68 mmol) of cyclo-$(Me_2SiNMe)_2$ was added. The mixture was warmed to -15°C, at which point the cyclodisilazane dissolved. After 10 min trimethylchlorosilane (2.14 g, 19.7 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. Standard workup showed the presence of n-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ in 87% yield. The product had proton NMR and IR spectra identical with those of an authentic sample (see above).

(b) Vinyldimethylchlorosilane Quench

Essentially the same procedure as in (a) was used, except that only 10% of the cyclo-$(Me_2SiNMe)_2$ was added at -78°C and the rest at -15°C. Also, $ViMe_2SiCl$ was used in place of Me_3SiCl. The product, n-$BuMe_2SiNMeSiMe_2NMeSiMe_2Vi$, was obtained in 68% yield.

Anal. Calcd. for $C_{14}H_{36}N_2Si_3$: C, 53.09; H, 11.46; N, 8.84. Found: C, 52.92; H, 11.46; N, 9.23.

^1H NMR (250 MHz, $CDCl_3$): δ 0.04 (s, 6H, n-Bu$\underline{Me_2}$Si), 0.08 (s, 6H, $NSiMe_2N$), 0.13 (s, 6H, Si$\underline{Me_2}$Vi), 0.54 (t, 2H, n-Pr$C\underline{H_2}$Si), 0.86 (t, 3H, CH_3 of n-Bu), 1.27(broad m, 6H, internal CH_2CH_2 of n-Bu), 2.4 (s, 6H, MeN), 5.6 - 6.3 (complex m, 3H, CH_2=CH)

Reaction of cyclo-$(Me_2SiNMe)_2$ with Methyllithium/Sodium t-Butoxide.

(a) Trimethylchlorosilane Quench

The same procedure was used as in (b) immediately above except that methyllithium in Et_2O was used in place of n-BuLi and Me_3SiCl was the chlorosilane added. The product, $Me_3SiNMeSiMe_2NMeSiMe_3$, a known compound (see above), was obtained in 70% yield. Its ^1H NMR spectrum was identical with that reported above.

(b) Vinyldimethylchlorosilane Quench

The same procedure as that was described immediately above was used, except that $ViMe_2SiCl$ was the chlorosilane used. The product, $Me_3SiNMeSiMe_2NMeSiMe_2Vi$, was obtained in 60% yield.
Anal. Calcd. for $C_{11}H_{30}N_2Si_3$: C, 48.10; H, 11.00; N, 10.20. Found: C, 48.09; H, 11.17; N, 10.55.
^1H NMR (250 MHz, $CDCl_3$): δ 0.05 (s, 9H, Me_3Si), 0.08 (s, 6H, $NSiMe_2N$), 0.13 (s, 6H, $SiMe_2Vi$), 2.4 (s, 6H, MeN) 5.6 - 6.3 (complex m, 3H, CH_2=CH).

Reaction of cyclo-$(Me_2SiNMe)_2$ with Methyllithium/Potassium t-Butoxide.

The standard apparatus was charged with 1.04 g (9.27 mmol) of t-BuOK and 30 ml of THF. To this solution, cooled to -78°, was added 17.0 ml of a 0.545M solution of MeLi in Et_2O (9.27 mmol). After 5 min, one-tenth of a solution of 1.645g (9.43 mmol) of cyclo-$(Me_2SiNMe)_2$ was added by syringe. The mixture then was warmed to -15°C and the rest of the cyclodisilazane solution was added. The resulting mixture was warmed to room temperature and now 1.20 g (11.1 mmol) of Me_3SiCl was added. After 30 min., the standard workup gave 3.26 g of a clear, very viscous oily solid. This was diluted with THF and trap-to-trap distilled to give 2.1 g of a clear, yellowish liquid. GLC analysis showed $Me_3SiNMeSiMe_2NMeSiMe_3$ (see above) to be present in 60% yield.

Ring-Opening Polymerization of cyclo-$(Me_2SiNMe)_2$

(1) With Organolithium Reagents.

The general procedure was as follows.

The standard reaction apparatus was charged with the solvent, cooled (either to 0°C or -78°C) and then the $(Me_2SiNMe)_2$ was added by syringe. Subsequently, the organolithium reagent solution was added and the reaction mixture was stirred at room temperature and then at the reflux temperature for some hours. The chlorosilane, generally an excess, then was added to "kill" the living polymer (LiCl precipitated) and the mixture was stirred at room temperature for 30-60 min. Volatiles were removed at reduced pressure, leaving a white solid which then was extracted with 15-20 ml of hexane. The extracts were centrifuged to remove LiCl and the supernatant solution was distilled (trap-to-trap in vacuo), leaving, generally, a white, waxy solid. The latter was soluble in organic solvents such as hexane, benzene, chloroform, carbon tetrachloride and THF.

(a) 10% MeLi in THF.

Hexamethylcyclodisilazane (1.546 g, 8.9 mmol) and 0.66 ml of 1.35M (0.89 mmol) of MeLi in diethyl ether were allowed to react in 25 ml of THF (2.5 h. reflux). Trimethylchlorosilane (0.26 g, 2.4 mmol) was added. Work-up gave 1.148 g (75% yield) of a white, waxy solid.

Anal. Calcd: C, 42.33; H, 10.66; N, 14.81. Found: C, 40.65; H, 9.85; N, 14.02.

^1H NMR (250 MHz, $CDCl_3$): δ 0.11 (s, 2.2H, SiMe) 2.39 (s, 1 H, NMe). ^{29}Si NMR(59.59 MHz, DEPT, $CDCl_3$): δ_{Si} -2.18 (s, $SiMe_2$), -1.4 ($Me_3SiNMeSiMe_2$-), 5.2 (s, $SiMe_3$).

Mol. wt. (cryoscopy): 1140 (calcd. from monomer/ RLi ratio: 1735)

(b) 5% Methyllithium in THF.

$(Me_2SiNMe)_2$ (1.743 g, 9.99 mmol) and 0.39 ml of 1.30M MeLi (0.51 mmol) in Et_2O were allowed to react in 25 ml of THF (mixed at -78°C, at reflux for 4 h); 1.72 g (15.8 mmol) of Me_3SiCl was added. Work-up gave a white, waxy solid (1.65 g, 94% yield).

Mol. wt. (cryoscopy): 3000 - 3200 (calcd. from monomer/RLi ratio: 3400).

(c) 5% n-Butyllithium in THF

$(Me_2SiNMe)_2$ (0.468 g, 2.68 mmol) and 53ml of 2.52M (0.13 mmol) of n-BuLi in hexane were allowed to react in 25 ml of THF, initially at -78°C, then, after slow warming, at reflux for 1 h. Dimethylchlorosilane (20 mg, 0.18 mmol) was added. Work-up gave 0.414 g (89%) of a white, waxy solid.
Anal. Calcd: C, 41.80; H, 10.00; N, 14.82. Found: C, 40.78; H, 9.39; N, 14.59.
^1H NMR (300 MHz, C_6D_6): δ 0.36 (s, 2H, SiMe), 2.56 (s, 1H, NMe).
^{13}C NMR (67.9 MHz, C_6D_6): δ_C 1.94 (q, J = 118.3Hz, SiMe), 30.25 (q, J = 136.0 Hz, NCH_3). ^{29}Si NMR (59.59 MHz, DEPT, C_6D_6): δ_{Si} -1.82.
Mol. Wt.(VPO): 1500.

(d) 10% n-Butyllithium in Hexane.

$(Me_2SiNMe)_2$ (1.831 g, 10.5 mmol) and 0.45 ml of 2.42M (1.1 mmol) of n-BuLi in hexane were allowed to react in 30 ml of hexane (initially at 0°C, then at reflux for 1 h). Trimethylchlorosilane (23.7 mmol) was added. Work-up gave 1.67 g (91%) of a white, waxy solid.
^1H NMR (250 MHz, $CDCl_3$): δ 0.12 (s, 6.2H, SiMe), 0.4 - 1.25 (complex m, 1H, C_4H_9), 2.39 (s, 2.8H, NMe).
Mol. Wt. (cryoscopy): 1020 (calcd: 1680).

(2) With the RLi/Me_3CONa Reagent.

The standard reaction apparatus was charged with the sodium tert-butoxide and the THF and the solution was cooled to -78°C. Subsequently, an equimolar quantity of the organolithium reagent was added and the mixture was stirred at -78°C for a few minutes. One-tenth of the total amount of the $(Me_2SiNMe)_2$ to be added then was introduced by syringe. The Dry Ice/acetone bath was removed and the rest of the cyclodisilazane was added at -15°C over a period of 10 min. The reaction mixture was allowed to warm to room temperature and then an excess of a chlorosilane was added. After 30 min of stirring the volatiles were removed at reduced pressure. The residue was extracted with hexane. Centrifugation and removal of hexane at reduced pressure generally left a white waxy solid.

(a) 10% MeLi/Me_3CONa

$(Me_2SiNMe)_2$ (2.036 g, 11.67 mmol), 0.11g (1.14 mmol) of Me_3CONa and 2.1 ml of 1.35 M (1.14 mmol) of MeLi in Et_2O were allowed to react in 25 ml of THF, initially at -78°C, then at room temperature. Trimethylchlorosilane (2.37 mmol) was added. Work-up gave 1.737 g (85%) of a white, waxy solid.
Anal. Calcd: C, 41.96; H, 10.56; N, 15.29; Si, 32.19. Found: C, 40.95; H, 9.38; N, 13.89; Si, 33.18.
^1H NMR (250 MHz, $CDCl_3$): δ 0.12 (s, 2.15H, SiMe), 2.39 (s, 1H, NMe). ^{29}Si NMR (59.59 MHz, DEPT, $CDCl_3$): δ_{Si} -2.25 (s, inner $SiMe_2$), -1.53 (s, $Me_3SiNMeSiMe_2$-), 5.17 (s, $SiMe_3$).
Mol. Wt. (cryscopy): 1425 -1500 (calcd: 1780). Ceramic yield (by TGA, to 950°C at 10°C/min. under argon): 0%.

In another such experiment, the living polymer was quenched with $Me_2(CH_2{=}CH)SiCl$ to give a polymer with a $SiMe_2CH{=}CH_2$ end-group as a white, waxy solid in 97% yield, mol. wt. 1960.

(b) 10% n-BuLi/Me_3CONa

$(Me_2SiNMe)_2$ (0.90 g, 5.2 mmol), 0.05 g (0.52 mmol) of Me_3CONa and 0.20 ml of 2.57M (0.52 mmol) of n-BuLi in hexane were allowed to react in 30 ml of THF, initially at -78°C, then at room temperature. Trimethylchlorosilane (0.13 g, 0.12 mmol) was added. Work-up gave 0.833 g (93%) of a white, waxy solid.

Anal. Calcd: C, 42.94; H, 10.65; N, 14.95. Found: C, 41.91; H, 10.03; N, 14.03.

^1H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 2H, SiMe), 2.40(s, 1H, NMe); (400 MHz, C_6D_6): δ 0.35 (s, 2H, SiMe), 2.56 (s, 1H, NMe). ^{29}Si NMR (59.59 MHz, DEPT, $CDCl_3$): δ_{Si} -2.25; in C_6D_6, δ_{Si} -1.79.

Mol. Wt. (cryoscopic): 1580 (calcd. 1730).

A similar reaction in which $Me_2(CH_2=CH)SiCl$ was used in place of Me_3SiCl gave a white, waxy solid, molecular weight around 1550.

(c) 5% n-BuLi/Me_3CONa

The same procedure as above was used except that 5% n-BuLi/Me_3CONa (0.25 mmol/4.9 mmol of $(Me_2SiNMe)_2$) was used. A white, tacky solid (0.875 g, 100%) was obtained.

Anal. Calcd: C, 42.18; H, 10.53; N, 15.47. Found: C, 42.31; H, 9.89; N, 15.12.

^1H NMR(300 MHz, $CDCl_3$): δ 0.12 (s, 2H, SiMe), 2.40 (s, 1H, NMe); (400 MHz, C_6D_6): δ 0.36 (s, 2H, SiMe), 2.56 (s, 1H, NMe). ^{29}Si NMR (59.59 MHz, $CDCl_3$): δ_{Si} -2.27 (in C_6D_6, -1.79).

Reaction of cyclo-$(Me_2SiNMe)_2$ with 20% n-Butyllithium/Potassium tert-Butoxide in THF, Trimethylchlorosilane Quench

The standard reaction apparatus was charged with potassium tert-butoxide 0.054 g, 0.50 mmol) in the dry box, connected to a nitrogen line, and cooled to -78°C in a dry ice/acetone bath. By syringe, 15 ml of THF was added and then 0.21 ml of a 2.40 M solution of n-butyllithium (0.50 mmol) in hexane was added. After 5 min, cyclo-$(Me_2SiNMe)_2$ (0.428 g, 2.45 mmol) was added all at once. The cyclodisilazane was frozen in the reaction mixture. The bath was removed and the reaction mixture warmed until the

cyclodisilazane dissolved. The -78°C bath was replaced and the reaction mixture cooled again to -78°C. A GLC analysis of the reaction mixture showed no remaining cyclodisilazane, so trimethylchlorosilane (0.13 g, 1.20 mmol) was added and the bath was removed. The reaction mixture was warmed to room temperature and a white precipitate formed. The standard work-up was done. A GLC analysis (internal standard C_9) of the reaction mixture showed the presence of one major product, $(Me_2SiNMe)_3$ (0.40 g, 1.5 mmol, 94% based on the conversion of three equivalents of the cyclodisilazane to two equivalents of the cyclotrisilazane), which was identified by comparison of its ^1H NMR spectrum and melting point (34°C, lit.[12] 33-34°C) with those of an authentic sample.

Reaction of cyclo-$(Me_2SiNMe)_2$ with 10% KH in THF

The standard reaction appartus was charged with 30 ml of THF and 0.02 g of KH (0.5 mmol). By syringe cyclo-$(Me_2SiNMe)_2$ (0.892 g, 5.11 mmol) was added over 20 min. After an additional 1h at room temperature, the KH was still present as an insoluble solid in the reaction mixture which settled rapidly when the reaction mixture was not stirred. A GLC analysis of the supernatant solution showed that cyclo-$(Me_2SiNMe)_2$ had completely reacted and a new product was present. Methyl iodide (1.0 ml, 2.28 g, 16.2 mmol) was added. No precipitate formed. A standard work-up of the reaction mixture was performed to remove the unreacted KH. The GLC analysis (internal standard C_{10}) of the reaction mixture showed the presence of one major product, cyclo-$(Me_2SiNMe)_3$ (0.895 g, 3.42 mmol, 89% based on the conversion of three equivalents of the cyclodisilazane to two equivalents of the cyclotrisilazane), which was GC-collected and identified by comparison of its ^1H NMR spectrum and melting point (34°C; lit[12] 33-34°C) with those of an authentic sample. Another lower-boiling minor product was also present by GLC analysis, but in a quantity too small to collect and identify.

Attempted Polymerization of cyclo-$(Me_2SiNPr^i)_2$ with 5% Methyllithium in THF, Trimethylchlorosilane Quench.

The standard reaction appartus was charged with 20 ml of THF and 0.972 g of cyclo-$(Me_2SiN^iPr^i)_2$ (4.22 mmol) and the reaction mixture was heated to reflux. By syringe, 0.13 ml of a 1.59 M solution of methyllithium (0.21 mmol) in Et_2O was added. After an additional 18h at reflux, trimethylchlorosilane (0.030 ml, 0.026 g, 0.21 mmol) was added. A white precipitate formed. The standard work-up of the reaction mixture was performed. The GLC analysis (internal standard C_9) of the reaction mixture showed the presence of one major product, unreacted cyclo-$(Me_2SiNPr^i)_2$ (0.885 g, 3.84 mmol, 91%), which was identified by comparison of its ^1H NMR spectrum with that of an authentic sample.

The same result was observed when n-butyllithium was used in place of methyllithium.

Pyrolysis of a $Me(SiMe_2NMe)_xSiMe_3$ Polymer

A 4.604 g sample of the polymer (mol. wt. 1425-1500) was divided between two silica boats and pyrolyzed in a stream of nitrogen in a Lindberg tube furnace equipped with a controller (30° to 300°C at 10°C/min; 30 min at 300°; 300°C to 700°C at 10°C/min). The exit end of the pyrolysis tube led to two traps which were immersed in liquid nitrogen. Upon completion of the pyrolysis the tubes were found to contain white solids. These were dissolved in diethyl ether. Evaporation of most of the ether at reduced pressure left a concentrated solution of the volatile pyrolysis products. This solution was examined by GLC. Two products were present. These were collected and yields were determined (n-nonane internal standard): cyclo-$(Me_2SiNMe)_2$ (38% yield) and $(Me_2SiNMe)_3$ (12% yield). They were identified by comparison of their IR and ^1H NMR spectra with those of authentic samples.[12]

Acknowledgments The authors are grateful to the Office of Naval Research for support of this work.

REFERENCES AND NOTES

1. Noll, W. "Chemistry and Technology of Silcones", Academic Press: New York, 1968, Chapter 5.

2. For a discussion of previous attempts to prepare linear polysilazanes containing R_2SiNR or R_2SiNH repeat units see: Aylett, B.J. Organomet. Chem. Rev. 1968, 3, 151.

3. Seyferth, D. in "Inorganic and Organometallic Polymers", (ACS Symposium Series 360), Zeldin, M.; Wynne, K.J.; Allcock, H.R., eds., American Chemical Society: Washington, D.C., 1988, pp. 143-155 and references cited therein.

4. Michalczyk, M.J.; Fink, M.J.; Haller, K.J.; West, R.; Michl, J. Organometallics 1986, 5, 531.

5. For reviews on cyclodisilazanes see:
   (a) Fink, W. Angew Chem. Int. Ed. Engl. 1966, 5, 760
   (b) Zhinkin, D.Ya., Varezhkin, Yu.M.; Morgunova, M.M. Russ. Chem. Rev. 1980, 49, 1149.
   (c) Varezhkin, Yu.M.; Zhinkin, D.Ya; Morgunova, M.M. Russ Chem Rev. 1981, 50, 1158.
   (d) Klingebiel, U. Nachr. Chem. Tech. Lab. 1987, 35, 1042.

6. Gergo, E.; Schultz, G.; Hargittai, T. J. Organomet. Chem. 1985, 292, 343.

7. (a) Parkanyi, L.; Argay, G.; Hencsei, P.; Nagy, J. J. Organomet. Chem. 1976, 116, 299.
   (b) Parkanyi, L.; Szollosy, A.; Bihatsi, L., Hencsei, P. J. Organomet. Chem. 1983, 251, 159.
   (c) Parkanyi, L.; Szollosy, A.; Bihatsi, L; Hencsei, P.; Nagy, J. J. Organomet. Chem. 1983, 256, 235.

(d) Parkanyi, L.; Bihatsi, L.; Hencsei, P.; Szollosy, A. J. Organomet. Chem. 1987, 321, 7.

8. (a) Bush, R.P.; Lloyd, N.C.; Pearce, C.A. J. Chem. Soc. Chem. Commun. 1967, 1269.
(b) Bush, R.P.; Pearce, C.A. J. Chem. Soc. (A) 1969, 808.

9. Fink, W. Chem. Ber. 1963, 96, 1071.

10. Williams, E.A., Cargioli, J.D., in Annual Reports on NMR Spectroscopy, Vol. 9, Webb, G.A., Ed., Academic Press, New York, 1979, pp. 221-318; Vol 15, 1983, pp. 235-289.

11. Lochmann, L.; Pospisil, J.; Lim, D. Tetrahedron Lett. 1966, 257.

12. Breed, L.W.; Elliott, R.L. Inorg. Chem. 1964, 3, 1622.

13. Wannagat, U.; Schreiner, G. Monatsh. Chem. 1965, 96, 1916.

14. Rochow, E.G.; Lienhard, K. Z. Anorgan Allg. Chem. 1964, 331, 316.

15. Wiseman, G.H.; Seyferth, D.; Wheeler, D.R. Organometallics 1986, 5, 146.

TABLE 1. Stoichiometric Ring Opening of cyclo-$(Me_2SiNMe)_2$ and (cyclo-$Me_2SiNPr^i)_2$ by Organoalkali Reagents.

I. Reactions of cyclo-$(Me_2SiNMe)_2$

RLi	Chlorosilane Quench	Product (% Yield)
MeLi	Me_3SiCl	$Me_3SiNMeSiMe_2NMeSiMe_3$ (70)
MeLi	Me_2HSiCl	$Me_3SiNMeSiMe_2NMeSiMe_2H$ (83)
MeLi	Me_2SiCl_2	$Me_3SiNMeSiMe_2NMeSiMe_2Cl$ (57)
n-BuLi	Me_3SiCl	n-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ (81)
n-BuLi	Me_2HSiCl	n-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ (86)
t-BuLi	Me_3SiCl	t-$BuMe_2SiNMeSiMe_2NMeSiMe_3$ (87)
t-BuLi	Me2HSiCl	t-$BuMe_2SiNMeSiMe_2NMeSiMe_2H$ (80)
MeLi/Me_3CONa	Me_3SiCl	$Me_3SiNMeSiMe_2NMeSiMe_3$ (70)
MeLi/Me_3CONa	$Me_2ViSiCl$	$Me_3SiNMeSiMe_2NMeSiMeVi$ (60)
MeLi/Me_3COK	Me_3SiCl	$Me_3SiNMeSiMe_2NMeSiMe_3$ (60)

II. Reactions of cyclo-$(Me_2SiNPr^i)_2$

MeLI	Me_2HSiCl	$Me_3SiNPr^iSiMe_2NPr^iSiMe_2H$ (64)
n-BuLi	Me_2HSiCl	n-$BuMe_2SiNPr^iSiMe_2NPr^iSiMe_2H$ (67)

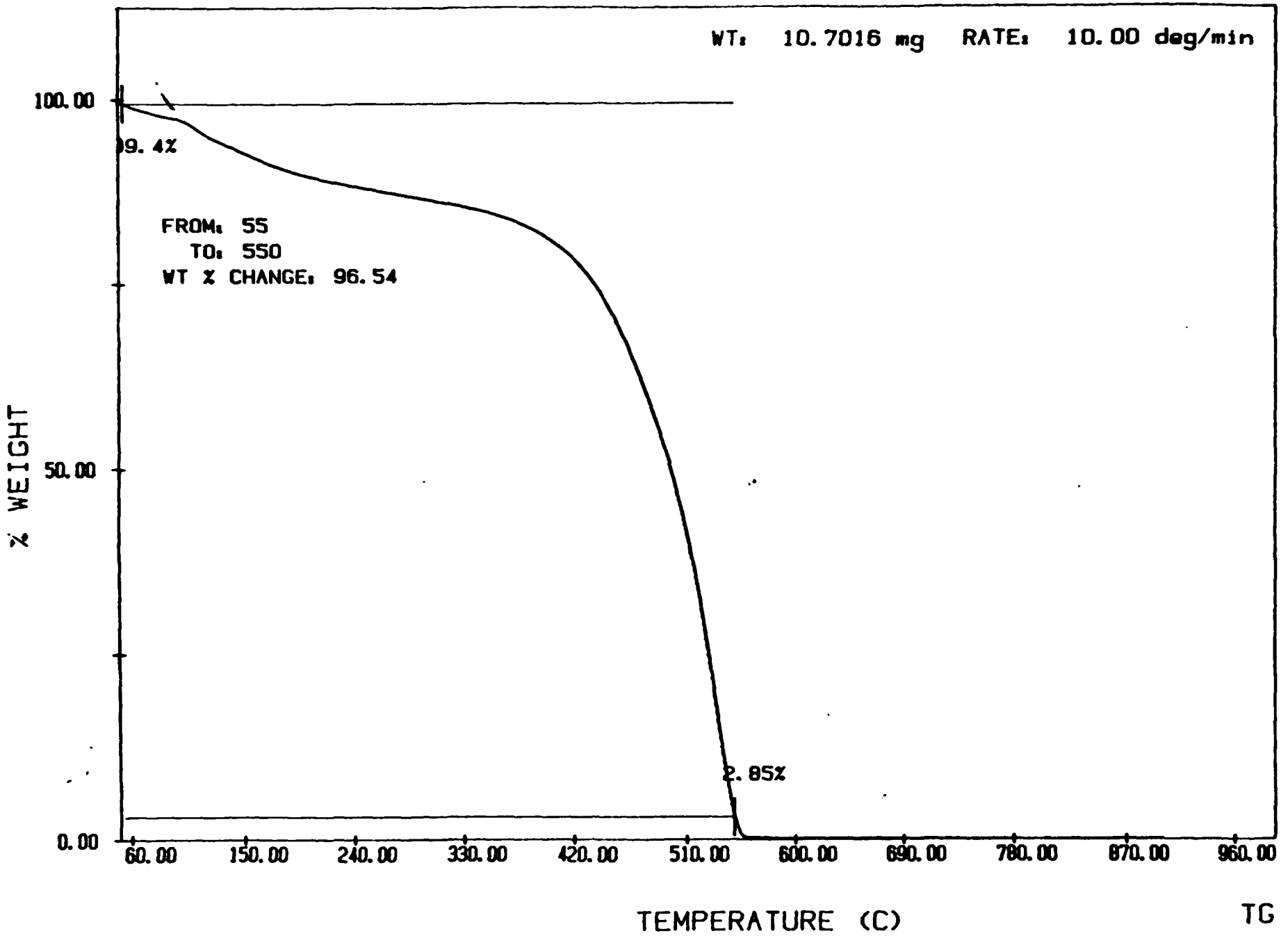

WT: 10.7016 mg RATE: 10.00 deg/min
100.00
50.00
0.00
% WEIGHT
9.4%
FROM: 55
TO: 550
WT % CHANGE: 96.54
2.85%
60.00
150.00
240.00
330.00
420.00
510.00
600.00
690.00
780.00
870.00
960.00
TEMPERATURE (C)
TG

Fig. 1

DL/1113/89/1

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	No. Copies
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 high quality
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1

POLYMER PROGRAM DISTRIBUTION LIST

Dr. J. M. Augl
Naval Surface Weapons Center
White Oak, MD 20910

Dr. A. S. Abhiraman
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

4132033

Dr. Harry R. Allcock
Department of Chemistry
Pennsylvania State University
University Park, PA 16802

4132007

Dr. Chris W. Allen
Department of Chemistry
University of Vermont
Burlington, VT 05405

413c012

Dr. Ronald D. Archer
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

413c028

Dr. Ali S. Argon
Mechanical Engineering Department
Massachusetts Institute of Technology
Cambridge, MA 02139

a400005df

Dr. William J. Bailey
Department of Chemistry
University of Maryland
College Park, MD 20742

413a006

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Avenue
Azusa, CA 91702

4000021sbi

Dr. Frank D. Blum
Department of Chemistry
University of Missouri - Rolla
Rolla, MO 65401

413m005

Dr. Len J. Buckley
Naval Air Development Center
Code 6063
Warminster, PA 18974

Dr. F. James Boerio
Materials Science & Engineering Dept.
University of Cincinnati
Cincinnati, Ohio 45221

413m012

Dr. Ivan Caplan
DTNSRDC Annapolis
Code 0125
Annapolis, MD 21401

Dr. Robert E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

4132001

Dr. E. Fischer
DTNSRDC Code 2853
Annapolis, MD 21402

Dr. Curtis W. Frank
Department of Chemical Engineering
Stanford University
Stanford, CA 94305

413h005

Dr. Gregory S. Girolami
School of Chemical Sciences
University of Illinois
Urbana-Champagne, IL 61801

4132014

Dr. Robert H. Grubbs
Department of Chemistry
California Institute of Technology
Pasadena, CA 91124

4132019

Dr. James F. Haw
Department of Chemistry
Texas A&M University
College Station, TX 77843

413c039

Dr. Stuart L. Cooper
Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

4132006

Dr. Warren T. Ford
Department of Chemistry
Oklahoma State University
Stillwater, OK 74078

413h006

Dr. John K. Gillham
Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08544

413c005

Dr. Bernard Gordon
Department of Polymer Science
Pennsylvania State University
University Park, PA 16802

413c025

Dr. Henry K. Hall
Department of Chemistry
University of Arizona
Tucson, AZ 85721

413j009

Dr. Alan J. Heeger
Department of Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

4132012

Dr. Pat J. Hendra
Department of Chemistry
University of Southampton
Highfield Southampton 509 5NH
United Kingdom
4134001

Dr. Charles E. Hoyle
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

413c026

Dr. Bruce S. Hudson
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

413c018

Dr. Leonard V. Interrante
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12181

413c014

Dr. Hatsuo Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

413m008

Dr. Jeffrey T. Koberstein
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

4132013

Dr. Paul M. Lahti
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

413c037

Dr. Richard M. Laine
Washington Technology Center
University of Washington
Seattle, WA 98195

s400033srh

Dr. Robert W. Lenz
Polymer Science and Engineering Dept.
University of Massachusetts
Amherst, MA 01002

441c013

Dr. Geoffrey Lindsay
Chemistry Division - Code 087
Naval Weapons Center
China Lake, CA 93555

4132036

Dr. Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104

a400004df

Dr. Chris W. Macosko
Materials Science & Engineering Dept.
University of Minnesota
Minneapolis, MN 55455

4132029

Dr. Joseph H. Magill
Materials Science & Engineering Dept.
University of Pittsburgh
Pittsburgh, PA 15161

413c013

Dr. Leo Mandelkern
Department of Chemistry
Florida State University
Tallahasee, FL 32306-3015

4132018

Dr. Tobin J. Marks
Department of Chemistry
Northwestern University
Evanston, IL 60201

413c030

Dr. Lon J. Mathias
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 30406-0076

413m003

Dr. Krzysztof Matyjaszewski
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

413j002

Dr. James E. McGrath
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132007

Dr. William B. Moniz
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

4132012

Dr. Kay L. Paciorek
Ultrasystems Defense and Space, Inc.
16775 Von Karman Avenue
Irvine, CA 92714

s400029srh

Dr. Virgil Percec
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

413c024

Dr. Martin Pomerantz
Department of Chemistry
University of Texas at Arlington
Box 19065
Arlington, TX 76019-0065
a400008df

Dr. Roger S. Porter
Dept. of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01002

413m006

Dr. T. J. Reinhart, Jr.
Nonmetallic Materials Division
Air Force Materials Laboratory (AFSC)
Wright-Patterson AFB, OH 45433

Dr. Arnost Reiser
Insitute of Imaging Sciences
Polytechnic University
333 Jay Street
Brooklyn, NY 11021

4132022

Dr. Ferdinand Rodriguez
Department of Chemical Engineering
Cornell University
Ithaca, NY 14853

413c011

Dr. Charles M. Roland
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

413m009

Dr. Michael F. Rubner
Materials Science & Engineering Dept.
Massachusetts Institute of Technology
Cambridge, MA 02139

413m007

Dr. Ronald Salovey
Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90089

413m010

Dr. Jacob Schaefer
Department of Chemistry
Washington University
St. Louis, MO 63130

413m001

Dr. Jerry I. Scheinbeim
Dept. of Mechanics & Materials Science
Rutgers University
Piscataway, NJ 08854

4132009

Dr. Lawrence R. Sita
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

4132030

Dr. L. E. Sloter
Code Air 931-A
Naval Air Systems Command
Washington, D. C. 20361-9310

Dr. Richard R. Schrock
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

4132038

Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

413c004

Dr. David S. Soane
Department of Chemical Engineering
University of California, Berkeley
Berkeley, CA 94720-9989

413h004

Dr. Les H. Sperling
Materials Research Center #32
Lehigh University
Bethlehem, PA 18015

413c002

Dr. Richard S. Stein
Polymer Research Institute
University of Massachusetts
Amherst, MA 01002

4132008

Dr. C. S. Sung
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

413m011

Dr. Sukant K. Tripathy
Department of Chemistry
University of Lowell
Lowell, MA 01854

4132016

Dr. C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

413c020

Dr. Kenneth B. Wagener
Department of Chemistry
University of Florida
Gainesville, FL 32611

a400007df

Dr. Robert A. Weiss
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06268

a400006df

Dr. George M. Whitesides
Department of Chemistry
Harvard University
Cambridge, MA 02138

4132010

Dr. Garth L. Wilkes
Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132020